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(54) Title: COMBUSTION SYNTHESIS OF SINGLE WALLED NANOTUBES

(57) Abstract: A method and apparatus for manufacturing single-walled nanotubes are disclosed. The method comprises providing a carbon-containing feed gas, adding a catalyst-containing or catalyst-precursor-containing gas or liquid to the feed gas, providing an oxygen-containing gas, and mixing the feed gas and the oxygen containing gas in a combustion zone such that combustion occurs and the catalyst catalyzes formation of single-walled nanotubes from the feed gas.

COMBUSTION SYNTHESIS OF SINGLE WALLED NANOTUBES

RELATED APPLICATIONS

This application claims benefit of provisional application Serial No. 60/167,372, filed November 24, 1999, and entitled "Combustion Synthesis Of Single Walled Nanotubes."

5   TECHNICAL FIELD OF THE INVENTION

The present invention relates generally to a method and apparatus for synthesizing single-walled nanotubes and more generally to a method for synthesizing in a flame. Still more particularly, the present invention relates to a technique for including a catalyst in a flame formed by combustion of a hydrocarbon in the presence of oxygen so as to allow the

10   formation of single-walled nanotubes.

BACKGROUND OF THE INVENTION

As used herein, "single-walled nanotubes" are composed substantially entirely of carbon atoms, arranged as a single rolled sheet of graphite, with diameter of ca. 1.4 nm and an aspect ratio (length/diameter) of at least 100.

15   Single-walled nanotubes (SWNTs) have generated much excitement in a variety of fields because of their unique properties. For example, SWNTs are the strongest material yet discovered, with a Young's modulus of ~1 TPa, and a shear modulus of ~0.5 TPa. Thus, they are under consideration as fiber reinforcements for all types of fiber-matrix composite materials, where the matrix could be carbon, ceramic, or metal. Some SWNTs also have

20   excellent transport properties, with a thermal conductivity greater than diamond and electrical conductivity greater than copper. These SWNTs can therefore be used to improve the conductivity of a non-conducting matrix, like polymers. As an example, this could be useful for static electricity reduction in relatively cheap parts in disk drives. Other SWNTs have semiconducting properties; the distinction is based on the way the carbon atoms arrange

25   themselves in the tube. The semiconducting tubes have been studied for nanoscale electronic devices. Nanoscale SWNT-based devices already demonstrated include rectifiers, transistors, and diodes. Furthermore, they have excellent field-emission characteristics, which is leading to their incorporation as the active element in flat screen displays.

The foregoing list of properties and applications includes some items that can also be

30   performed with multi-walled nanotubes (MWNTs). Field-emitters, conductivity enhancers, and fiber reinforcements for composites can all be carried out by MWNTs, although SWNTs intrinsically have somewhat better properties, and perhaps much better properties if the abundant defects in MWNTs are also considered. It is expected that a few from this shorter

list of applications could be developed using whichever variety of tubes can be supplied in homogenous batches, at reasonable cost. The nanoscale electronics are solely the province of SWNTs.

For SWNTs to fulfill any of their promising applications, however, they will have to made in larger quantities and at lower prices than are currently available. The current process for industrial manufacture of SWNTs comprises electrical arcing of metal-doped graphite rods. This process is inherently a batch process and cannot be scaled up beyond ~100g/day. As a result, neither the quantities available nor the current price level can support a scale-up in the level of commercial usage of SWNTs. Hence, it is desired to provide a method and apparatus that can achieve a commercially useful volume and lower cost production of SWNTs.

While there are other types of carbon fibers known in the art, none have the desirable properties that are expected to be exhibited by SWNTs. The carbon (or graphite) fibers currently in use commercially, for applications ranging from advanced military aircraft to golf club shafts, are spun from strands of a highly viscous liquid (pitch or polyacrylonitrile) that have been extruded through a small hole, and then carbonized. They have diameters in the micron range, and little heed is paid to the atomic ordering of the carbon atoms. PAN or pitch fibers bear scant resemblance to SWNTs at the ten nanometer scale, and their physical and electronic properties are greatly divergent. Lacking the atomic precision of the SWNT, PAN and pitch fibers' strength is much lower on a weight basis, and they have no potential for molecular electronics applications.

Another type of carbon fiber that has been extensively researched is the vapor grown carbon fiber (VGCF, reviewed by Rodriguez, 1993). Amongst carbon fibers, VGCFs are most like SWNTs, both in size (though VGCFs are larger), and, especially, in formation mechanism. Though several mechanisms have been proposed, agreement has yet to be reached on a detailed formation mechanism for SWNTs. However, as the leading model for SWNT growth is similar to VGCFs, some discussion of VGCF growth and history is warranted. VGCFs are grown by decomposing a hydrocarbon on the surface of a metal particle that acts as a catalyst for both the decomposition of the hydrocarbon and the growth of the fiber. Much has been written about the formation mechanism of VGCFs, and only a few points are widely (but not universally) agreed upon. First, the hydrocarbon precursor lands on the metal surface and dehydrogenates. Second, the remaining carbon is somehow carried into the metal particle. Third, the carbon is precipitated out at a face of the particle

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that is not being used for catalytic dehydrogenation. This process continues, with the accumulating carbons forming a fiber, until the reaction environment is changed. VGCFs are always observed with the metal catalyst particle still attached.

Various apparatus for VGCF growth are known. A hydrocarbon gas is typically used

5   as the carbon source. All hydrocarbons are, in principle, suitable, although there are some important trends. Large ring systems, such as pyrene and the benzoflouranthenes, are much less efficient than smaller hydrocarbons. The most commonly used hydrocarbons for VGCF growth are acetylene, ethylene and benzene. In a research setting, the hydrocarbon is then flowed through a tube in a tube furnace, which contains the metal catalyst. The furnace

10   temperature is usually between 600 and 1200 C. The catalyst is typically located in a ceramic boat inside the furnace, and can be either powdered or a solid solution of metal suspended in a ceramic. Many ceramics have been used, but SiO_2 and Al_2O_3 are the most common. Alternatively, inorganic molecules serving as catalyst precursors can be flowed in from the same side of the tube as the hydrocarbon, condensing into metal clusters as heat is

15   applied to them. At an industrial scale, a counterflow vertical geometry has been employed, which allows the VGCFs to settle out in at the bottom of the reactor. Both hydrogen and sulfur-containing compounds (typically H_2S or thiophene) have been added in attempts to improve yield and/or reduce pyrolytic carbon content.

The arrangement of the carbon atoms in the VGCF varies, and can be indexed by the

20   angle (θ) between the fiber axis and the graphite planes that make up the fiber. For example, with $\theta = 90°$, the fiber is a series of short stacked graphitic carbon sheets with the graphite c-axis parallel to the direction of the fiber growth (the fiber axis). With $\theta = 0°$, the result is a MWNT, and intermediate θ gives the most common stacked, hollow frustum-shaped planes that look like chevrons under TEM examination. It has been suggested that the shape of the

25   catalyst particle's face that extrudes the fiber controls θ, but both experimental and theoretical evidence is limited. VGCF researchers observed MWNTs decades before the term "MWNT" was coined, and MWNTs were in commercial production by Hyperion Catalysts (as "carbon fibrils") at least a decade before carbon nanotubes were "discovered" by Ijima (1993). If there is one rather qualitative difference between the fibrils and most (but

30   by no means all) MWNTs, it is that the fibrils have more defects on average that the MWNTs. In any event, SWNTs were never observed in VGCF experiments, possibly because the VGCF catalytic metal particles were always too large and/or the carbon feed rates were incorrect.

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Since Ijima's paper (1993) stimulated the fullerene research community to action in nanotubes, a variety of new techniques have been added to the VGCF repertoire for filament growth. An electric arc between graphite rods was shown to produce MWNTs in the cathode deposit, or SWNTs when a metal catalyst was added (Iijima and Ichihashi, 1993; Bethune et al., 1993). Much literature has been devoted to optimizing the metals employed for catalysis. Currently, commercially available SWNTs are produced in arc synthesis technique. Arc synthesis of SWNTs is not any more economical than it was for fullerenes, however. At even higher cost, SWNTs can be grown in very high yield by dual-pulse laser ablation of a graphite/metal composite target in an inert atmosphere at ~1000°C.

More economically viable methods have also been developed for carbon nanotube synthesis, often closely approaching the methods investigated 10 - 20 years earlier for VGCF synthesis. In particular, decomposition of small hydrocarbons (CH_4, C_2H_2, C_2H_4, or CO) on supported or powdered metal catalysts particles of suitable diameter at elevated temperatures, typically 800 – 1200°C, have produced nanotubes, including SWNTs. Catalyst particles have been grown in the hydrocarbon gas feed, by decomposition of co-entrained organometallic precursors, such as ferrocene and iron pentacarbonyl, followed by nucleation of the metal atoms to form the particle. Like VGCFs, they have also been formed by controlled precipitation from a ceramic matrix. The typical experimental setup for these investigations is to flow the hydrocarbon through a tube furnace and collect the filaments out the back end. Both smaller catalysts and reduced hydrocarbon feed rates into the catalyst have been suggested to account for the formation of SWNTs instead of VGCFs.

Lastly, there are two reports of MWNT formation in a sooting flame, but SWNTs were not observed in either case (Duan and McKinnon, 1994; Howard et al., 1994). U.S. Patent No. 5,985,232, which is incorporated herein by reference, also discloses the formation of fullerenes in a sooting flame. A report of "large-scale" synthesis of SWNTs from an arc resulted in less than 2g of SWNTs. (Journet, C. et al., *Nature* 1997, 388, 756). A very recent report of "large-scale synthesis" by CVD produces 1g/day of SWNTs. (Colomer, J. et al. *Chem. Phys. Lett.* 2000, 317, 83). None of the above techniques have the potential to supply SWNTs in ton quantities.

Thus, there still remains a need for a high-volume, low-cost method and apparatus for producing SWNTs.

SUMMARY OF THE INVENTION

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The present invention includes a process for synthesizing single-walled carbon nanotubes (SWNTs) by combustion of fuel-rich hydrocarbon(s) in the presence of a metal catalyst. The quantities of SWNTs that can produced by the present catalyzed combustion synthesis method are expected to exceed tons/day, at prices below $100/lb (depending on yield).

More specifically, the present invention relates to a technique for incorporating at least one catalyst into the combustion mix in a manner that is effective to catalyze the formation of SWNTs. According to a preferred embodiment, the catalyst is provided in its gas phase and, as such, is mixed with the hydrocarbon feed prior to combustion. The gas stream containing the hydrocarbon(s) and the catalyst and the gas stream containing oxygen are kept separate until they are injected into the combustion zone. This is preferably achieved by providing one gas stream in a plurality of small diameter tubes bundled within a shell or conduit, with the second gas stream flowing through the shell, outside of the tubes. Alternatively, a first hydrocarbon stream is provided as fuel and a second hydrocarbon stream is injected into the flame that occurs when the first hydrocarbon stream is injected into the combustion zone and contacts the oxygen stream. According to the invention, catalyst can be provided in either hydrocarbon stream.

Downstream of the combustion zone, the combustion products, which may include soot along with the desired SWNTs, are collected and separated according to known techniques.

BRIEF DESCRIPTION OF THE FIGURES

For a more detailed description of the preferred embodiments of the invention, reference is now made to the accompanying Figures wherein:

Figure 1 is a schematic illustration of a fullerene-forming apparatus constructed in accordance with a preferred embodiment of the invention;

Figure 2 is an isometric view of a burner suitable for use in the fullerene-forming apparatus of Figure 1; and

Figure 3 is an alternative embodiment of a reactor suitable for use in the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring initially to Figure 1, one embodiment of a system for making SWNTs includes a reactor/combustion chamber 10, gas inlets 12 and 14, collection chamber 20, separator 30 and heat exchanger 40. Solids formed in combustion chamber 10, including

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soot and SWNTs, are collected in chamber 20 and then separated into their various' components in separator 30, as is known in the art. While combustion chamber 10 is depicted as vertical, with upward gas flow, other configurations are contemplated, including those in which combustion chamber 10 is horizontal, and those in which the flow through a

5   vertical chamber 10 is downward.

Fuel gas and oxygen or oxygen-containing gas are fed into combustion chamber 10 via gas inlets 12 and 14, respectively. Referring briefly to Figure 2, it is preferred that inlets 12 and 14 feed into a diffusion burner unit 15 that comprises a plurality of relatively small diameter tubes 16 bundled inside a larger tube 18. Fuel from inlet 12 is fed into tubes 16,

10   while oxygen or oxygen-containing gas from inlet 14 is fed into the channels 17 formed between tubes 16 and contained by tube 18. In this manner, the fuel gas and the oxygen-containing gas are kept separate until they are in the combustion zone. At the outlet end of diffusion burner unit 15, the gases from tubes 16 and channels 17 diffuse together in the combustion zone. Mass controllers or other suitable apparatus are preferably used to set the

15   flow rates of the oxygen and hydrocarbon gases.

According to a preferred embodiment, tubes 16 are 3/16" stainless steel tubes that are evenly spaced within a 4" diameter stainless steel tube 18. The oxygen-containing gas flows up through a metal frit (not shown) welded within the 4" tube, in the channels 15 defined between tubes 16. The fuel and oxygen diffuse rapidly into each other at the tips of the

20   3/16" tubes, and the flame has a homogeneous appearance.

While in one embodiment the excess fuel is used as the carbon source, in another embodiment the carbon source can be added independently. Separating the flame fuel from the carbon source allows the time-temperature history of the carbon for nanotubes to be decoupled from fuel requirements for burner stability. For example, carbon black plants

25   burn natural gas with air under slightly lean conditions to provide heat, but spray pitch in as   , the carbon source to make the blacks. The yield can then be optimized independently of the temperature and gas flows produced by the flame. To form SWNTs, carbon monoxide could be used as carbon source, with a conventional hydrocarbon being used as the fuel.

Referring now to Figure 3, an alternative embodiment 50 of the reactor of Figure 1

30   reflects the foregoing principle. Reactor 50 includes a combustion chamber 52, mixing zone 54, and reaction chamber 56. Hydrocarbon fuel and oxygen-containing gas are fed into combustion chamber 52 via inlets 51, 53, and form a flame, using any suitable commercial burner (not shown). Feed gas(es), including catalyst- or catalyst-precursor-containing gas or

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liquid are fed into the reactor between the flame and the mixing zone 54 and are mixed in mixing zone 54, after which they flow into reaction chamber 56.

Burner 59 is located at the inlet end of combustion chamber 52. The length of the combustion chamber must be long enough to allow complete reaction in the flame, but not so

5   long that excessive heat is lost through the section walls. In one embodiment, the combustion of methane and air will be conducted under stoichiometric conditions, such that essentially all of the gas is CO_2 and H_2O. This releases as much heat as possible from the methane. The adiabatic methane/air flame temperature is 2100°C, but can be lowered with the addition of additional nitrogen. That allows adjustment of the flame temperature. The

10   temperature of the SWNT formation reaction can be further adjusted by varying the methane flow rate. In another embodiment, the methane is incompletely combusted, that is, to CO and H_2. The CO can then be used as the source of carbon for SWNT growth.

It is preferred that the growth period for the SWNTs be approximately 50-100 milliseconds, after the catalyst and hydrocarbon are intimately mixed and before the reagents

15   cool below the reaction temperature. This is about ten times longer than the reaction time in arcs and lasers, and is expected to result in longer SWNTs. During the flow through this reaction zone, the temperature is most preferably held to be nearly constant, but adjustable over the range 800 - 1400°C.

It is preferred that turbulence be achieved in the gas flow in mixing zone 54 less than

20   one microsecond after the reagents (catalyst and hydrocarbon precursor) are injected into the reactor. Although turbulence can occur at lower Reynolds numbers due to geometry and injection effects. one preferred embodiment used flow with a Re > 10,000 to establish turbulence. Also, the diameter of the throat must not be so small that gas velocities through it are calculated to be sonic, which would not be a realistic operating condition. It is

25   relatively easy to achieve the desired flow conditions with the large gas flows present in commercial scale operations, but a very small throat was required for gas flows suitable for our laboratory apparatus.

Furthermore, in order to assure sample uniformity, it is not desirable for the gas flow in reaction chamber 56 to switch back to laminar. Laminar flow would result in a wide

30   dispersion in reaction times within a batch, leading to an inhomogeneous sample of SWNTs. At the same time, maintaining Re > 10,000 in this zone for one section would require unreasonably narrow diameters, resulting in the reaction being dominated by wall effects. It is therefore preferred to use a lower Reynolds number flow in reaction chamber 56, such as

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2,000 < Re < 10,000, particularly since the flow entering this section is already turbulent, and the section is unlikely to be long enough for fully developed laminar flow to occur. If longer reaction times are required, a longer reaction zone can be used.

5   The mixing section is where the reagents are added and turbulent gas flow is established. It is preferred that the reagents be injected in a manner that causes turbulence. As in a carbon black reactor, the reagents can be injected asymmetrically and radially at the beginning of the throat. This kind of injection helps to induce turbulence in the gas flow. As explained above, the length of the throat is set by the distance required for fully-developed turbulent flow. In order to maintain a more uniform temperature in the reaction zone,
10   additional heat (in the form of an electrical heat, e.g.) may be added at the back of the reaction section. The mixing section ends with a frustoconical diffuser 57, which helps eliminate eddies, and thus ensures uniformity of the SWNT product.

In a preferred embodiment, an optional cooling section 25 is included between combustion chamber 10, 50 and collection chamber 20. Cooling section 25 cools the solids-
15   containing gas stream down to a temperature that can be better tolerated by the collection bag.

The soot particles and SWNTs generated in either reactor apparatus are carried by the exhaust gas onto a ceramic filter bag 22 in collection chamber 20. As is known in the art of dust collection, the soot is shaken off of the bag periodically by a pulse jet system,
20   whereupon the soot falls down and can be collected out of the bottom of chamber 20. Alternatively, the soot can be blown into the inside of the bag(s) 22. Samples of the soot can be collected from the gas stream and removed from the apparatus during operation, for monitoring and control purposes or the like.

Regardless of whether the embodiment of Figure 1 or Figure 3 is used, preferred
25   fuels for use in the present invention include most hydrocarbons, although unsaturated hydrocarbons are preferred, with short-chain ($C_{<4}$) aliphatic hydrocarbons being most preferred. If it is desired to use hydrocarbon fuels that are liquid at ambient temperature and pressure, the liquid fuel can be fed to a boiler upstream of burner chamber 10 and the lines between the boiler and the burner can be heated, so as to provide the fuel to burner unit 15 as
30   a gas.

Metallocenes of Group VIIIa metals (specifically first-row elements) can be used as catalyst precursors for SWNT growth when they are sublimed into the flame. Subliming metallocenes makes it difficult to quantify the rate of metal addition to the reaction

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environment because of the competition between the metallocene decomposing and subliming at the high temperatures required for fast metal addition rates. Also, 10 carbon atoms, present in the cyclopentadiene rings, are added for every metal atom. The ring may not decompose fast enough to contribute to SWNT growth, and those carbons result in
5   additional soot instead, lowering the overall yield.

We have therefore identified several new catalyst precursor candidates. A liquid phase is desirable because it can be pumped, and thus accurately metered. The standard industrial choice for a liquid source of iron is iron pentacarbonyl, $Fe(CO)_5$. This is chemically very desirable for SWNT synthesis because the CO groups will readily release
10   the iron and will not contribute to soot. They may even provide an additional source of carbon for the SWNTs. An alternative liquid source of transition metals are the metal carboxylates with polyether linkages recently described by Walker, Jr., E.H., M.L. Breen and A.W. Apblett, *Preparation of Nickel Ferrite Using Liquid Metal Carboxylates*, Chem. Mater. 10, 1265-1269 (1998), which is incorporated herein by reference. Another route to
15   catalyst addition is to synthesize metal nanoparticles of the desired diameter as a colloidal suspension in a pumpable liquid. These are formed by the decomposition of the metal carbonyl in a heated solvent as described in Smith, T.W., and D. Wychick, *Colloidal Iron Dispersions Prepared via the Polymer-Catalyzed Decomposition of Iron Pentacarbonyl*, J. Phys. Chem. 84, 1821-1829 (1980), which is incorporated herein by reference. As the
20   catalyst precursor decomposes, the atoms of catalyst are freed and begin to agglomerate. If the reaction between the carbon and the catalyst particles is carefully controlled SWNTs are formed. If the catalyst particles are either too small, *i.e.* the reaction time is too short, or the catalyst agglomerates into particles that are too large, SWNTs are not formed and VGCFs or other carbon structures form. This method is expected to give excellent control over catalyst
25   particle size. It will be understood that catalyst suitable for use in the present method and apparatus can be added in an elemental, metallic, powdered, liquid or compounded form, without departing from the scope of the invention.

According to a preferred embodiment, transition metals, which are needed to catalyze the formation of meaningful amounts of SWNTs from carbon vapor, are introduced by
30   decomposing molecular precursors, which can be liquids or gases. Catalysts or catalyst precursors that are solid at ambient temperature can be sublimed to provide gaseous catalyst. For example, metallocenes can be sublimed from a packed bed. The temperature of the bed controls the vapor pressure of the metallocene and thus the addition rate for a given gas flow

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over the bed. The flowing gas can be any of the hydrocarbon streams, or an inert gas stream, but is preferably not an oxygen containing stream, as oxygen reacts with the catalyst precursor, rendering the catalyst ineffective.

Alternately, catalyst precursors that are liquid at ambient temperature and pressure,
5   such as bis(cyclo-pentadienyl)cobalt dicarbonyl (available from Strem Chemical), can be introduced by blowing argon over a reservoir of the liquid, and mixing the argon/metal compound vapor with the a desired stream downstream of the reservoir. Alternatively, the liquid can be pumped directly to the apparatus downstream of the flame, whereupon it evaporates and decomposes and provides catalyst particles. Iron pentacarbonyl,
10 cyclopentadienyl cobalt dicarbonyl are examples of liquid catalyst precursors that are suitable for use in the present invention. Other suitable catalysts include nickel carbonyl, which is a gas at room temperature.

Liquid or gaseous catalyst can be injected into the fuel feed line, the second hydrocarbon feed line, directly into the flame, or into the mixing region downstream of the
15 flame, depending on the apparatus used.

Example

In one preferred embodiment, 3.75 SLPM of acetylene was provided as fuel. Pure oxygen was used as the oxidizer and was fed at the rate of 4.5 SLPM, for an equivalence ratio of 1.7. A ferrocene/nickelocene mixture was used as catalyst precursors. Although it
20 has subsequently been discovered that higher pressures are more conducive to the formation of SWNTs, the pressure in combustion chamber 10 was maintained in this experiment at 80 torr. The collected soot was sonicated into methanol and suspended on a TEM grid (Structure Probe Inc.) for analysis. Despite the less than optimal reactor conditions, TEM images of the soot clearly showed SWNTs. Tubes in the soot were primarily single-walled.
25 While experiments on the preferred apparatus were carried out at low pressures (20 - 80 torr), as required for fullerene synthesis, it is believed that the optimum operating pressure for SWNT formation is higher, and may be one atmosphere or more. The best SWNT yields occurred at the highest pressures possible for the present apparatus, but is likely that the best embodiment of the combustion synthesis technique also occurs near ambient pressure.
30 One preferred carbon source that is suitable for use in the present invention is acetylene, which is also used in the manufacture of vapor grown carbon fibers. However, many small hydrocarbon molecules are probably suitable for SWNT growth using the present method, including methane, ethylene, ethane, propane, propene, etc. It may also be

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possible to employ a larger hydrocarbon that falls apart readily at high temperatures, which would have the potential advantage of handling a liquid rather than a gas. Examples of these would include hexane, hexene, tert-butane, and other aliphatic hydrocarbons, branched or unbranched. Less desirable are aromatic ring hydrocarbons, which derive special stability

5   from the ring, and are therefore less likely to undergo catalytic decomposition. Also, heteroatoms are valueless for SWNT formation. Examples of poor choices include benzene and its derivatives (such as toluene), naphthalene, amines, and pyridine.

It may also be possible to use the combustion exhaust gas itself as part of the carbon source for SWNTs, without adding any additional hydrocarbons. If so, the combustion

10   exhaust gas must be CO, instead of the product of complete combustion, CO_2, as CO_2 is too thermodynamically stable to participate in SWNT growth chemistry, except for the water-gas shift reaction, where it is converted into CO. CO, on the other hand, has been demonstrated to form SWNTs when flowed over a powdered metal catalyst at ~1200 K. Under conditions of incomplete combustion, the majority of the exhaust gas is CO and H_2. H_2 is occasionally

15   added to VGCF-forming processes to reduce the amorphous pyrolytic carbon (also called "thermal carbon" by Hyperion Catalysts, Inc.) that accumulates on the exterior of the carbon tube. While it seems ideal that combustion exhaust gases could be used as-is for SWNT growth, the rate of CO decomposition on the catalyst particles may not be competitive with that of hydrocarbons.

20   The optimum pressure and carbon feed per watt of heat for SWNT production can be determined experimentally and depend in part on the catalyst selected.

The present combustion synthesis technique allows SWNTs to be produced cheaply by a process that can be directly applied to tons/day production, based on analogy to carbon black manufacture. SWNTs have never previously been produced in a sooting flame. If

25   yields can be achieved that are similar to that of arcs or heated-tube pyrolysis, then combustion synthesis becomes the most economical method for the synthesis of SWNTs. Furthermore, the process would be very similar to already-existing carbon black plants, requiring little additional design. The additional metal catalyst required to form SWNTs will add to the cost, but otherwise, SWNTs can be made at costs similar to carbon black.

30   Specifically, it is expected that employing combustion synthesis at a pilot plant scale will drop the cost of SWNTs from ~$500/g to ~$50/lb (depending on yield).

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CLAIMS

What is claimed is:

1.   A method for manufacturing single-walled nanotubes, comprising:

    (a)   providing a carbon-containing feed gas;

    (b)   providing an oxygen-containing gas;

    (c)   adding a catalyst-containing or catalyst-precursor-containing gas or liquid to the feed gas; and

    (d)   mixing the feed gas and the oxygen containing gas in a combustion zone such that combustion occurs and the catalyst catalyzes formation of single-walled nanotubes from the feed gas.

2.   The method according to claim 1 wherein step (c) includes adding a catalyst containing precursor that has been sublimed or evaporated.

3.   The method according to claim 1 wherein step (d) includes decomposing a catalyst containing precursor and allowing freed catalyst atoms to agglomerate into catalyst particles.

4.   The method according to claim 1 wherein the feed gas and the oxygen containing gas are mixed before the or catalyst-precursor-containing gas or liquid is added to the feed gas.

5.   An apparatus for manufacturing single-walled nanotubes, comprising:

    a gas feed inlet;

    a catalyst feed inlet in communication with said gas feed inlet;

    an oxygen feed inlet that is not in communication with said gas feed inlet;

    a diffusion burner for receiving said gas feed inlet and said oxygen feed inlet and causing the gas feed and the oxygen feed to mix such that combustion occurs and the catalyst catalyzes formation of single-walled nanotubes from the feed gas.

6.   The apparatus according to claim 5, further including a system for subliming catalyst from a solid catalyst bed so as to provide gaseous catalyst to said catalyst feed inlet.

7.   The apparatus according to claim 3 wherein said system includes a heater and blower for

blowing hot gas across said catalyst bed.

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8.   The apparatus according to claim 5, further including a system for evaporating catalyst from a liquid catalyst reservoir so as to provide gaseous catalyst to said catalyst feed inlet.

5   9.   The apparatus according to claim 5 wherein said system includes a heater and blower for

blowing hot gas across said catalyst reservoir.

10.   The apparatus according to claim 5 wherein said diffusion burner comprises a

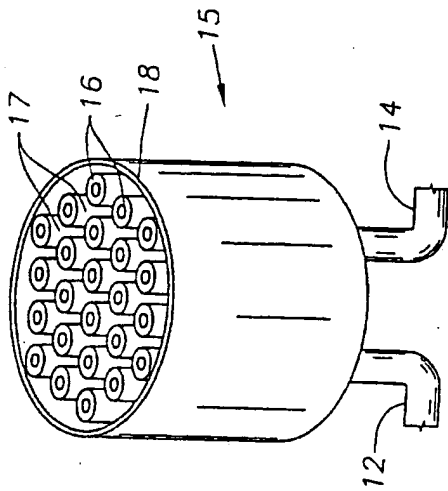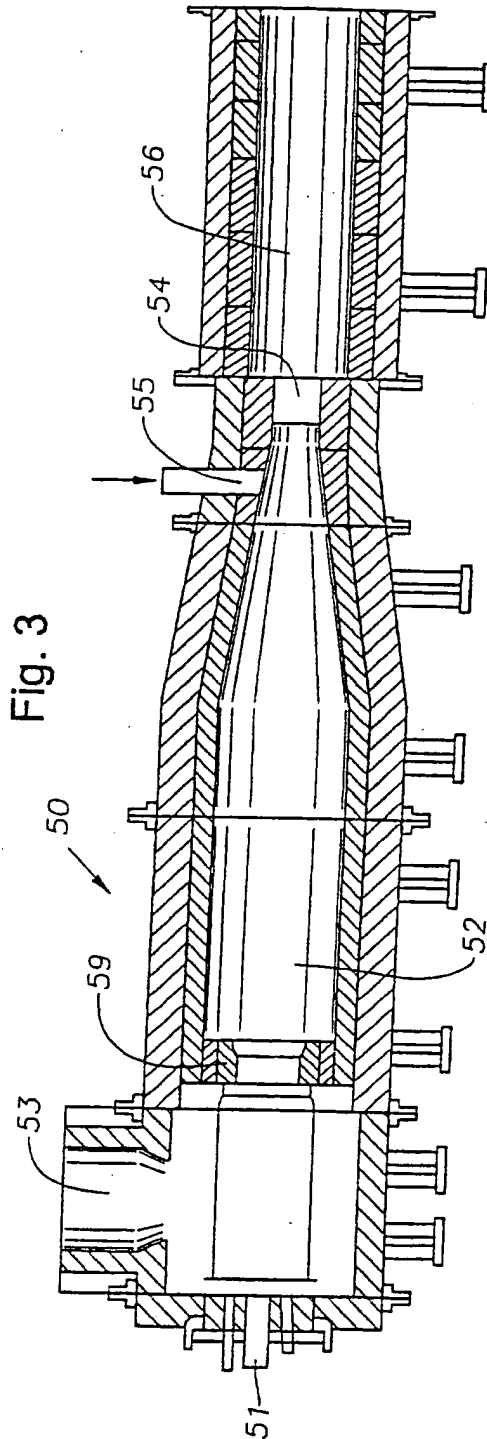10   plurality of smaller tubes bundled within a larger tube.

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Fig. 1
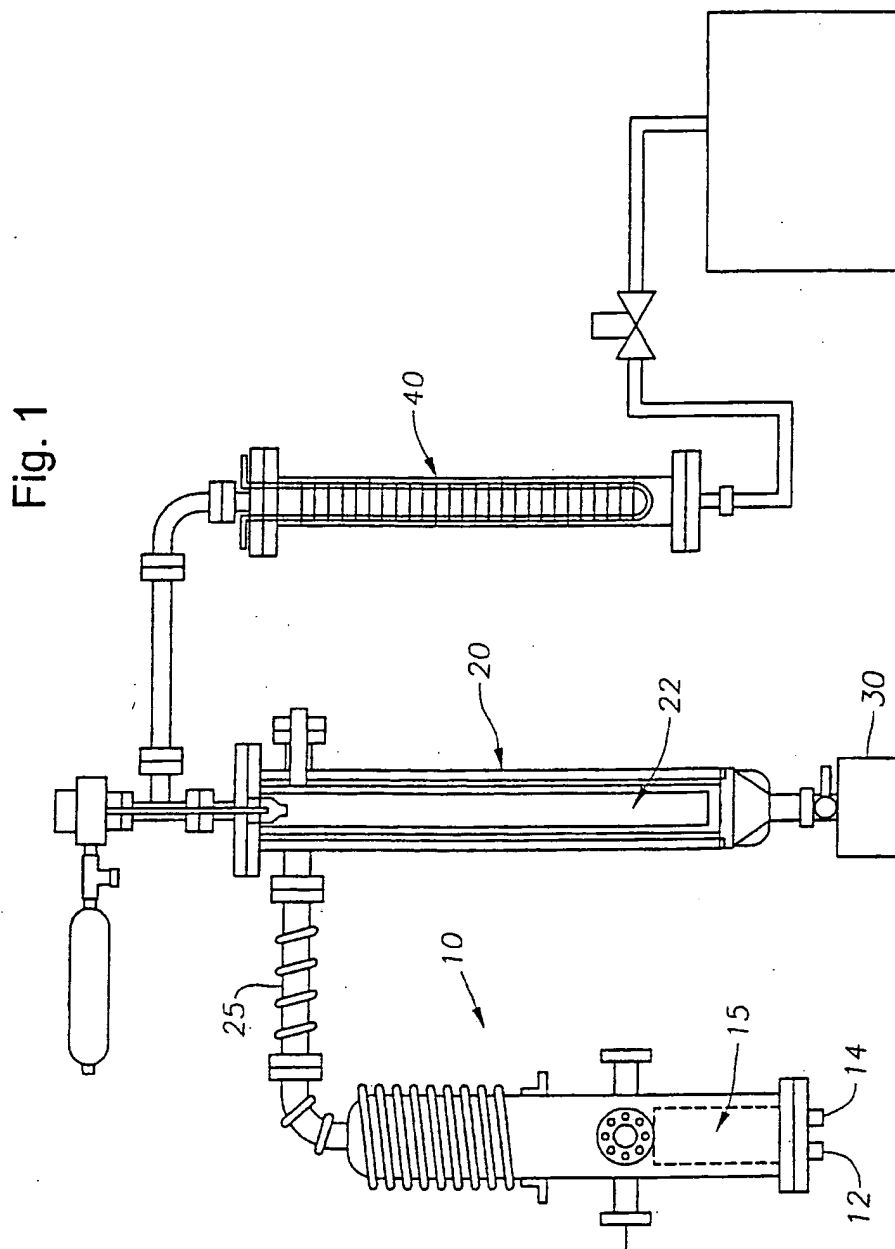
Fig. 2

Fig. 3

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : C01B 31/02
US CL   : 423/445B, 447.3
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :   423/445B, 447.3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SEN et al., 'Carbon Nanotubes by the Metallocene Route' Chemical Physics Letters Vol. 267 pgs. 276-280, 21 March 1997.	1-4
Y	JP 96-003636 A (HIDEKI YOSHIKAWA et al.), 01 September 1996, pg. 3.	1-4

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 FEBRUARY 2001	**12 MAR 2001**
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer STUART HENDRICKSON DEBORAH THOMAS PARALEGAL SPECIALIST Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)★

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/32213

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such
   an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

   Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable
   claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment
   of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers
   only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is
   restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
   1-4

Remark on Protest   ☐ The additional search fees were accompanied by the applicant's protest.

                               ☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1)) (July 1998)*

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

Group I, claim(s)1-4, drawn to a method.
Group II, claim(s) 5-10, drawn to an apparatus.
The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under
PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: There is no
special technical feature linking the claims: moreover, the apparatus contemplates the separate addition of catalyst feed
and gas feed. However, since the process recites adding both of these together, it appears that the apparatus does not
correspond to the process (and vice-versa).
   In that a common structure of an inlet and heated zone is common to both process and apparatus, it is noted that this
structure is old and known, and thus not a 'special technical feature' required for unity to exist.